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TSR 1-6777

DETERMINE THE PROPERTIES OF SEVEN LAYER OXYGEN BARRIER SHRINK FILMS

BOND STRENGTH (INSTRON) AT 73 DEG.F.

SAMPLE LBS/INCH

FDX 1570 BETWEEN LAYER 1 AND 2AVERAGE SPLIT OFF
STD.DEV.
* 95% C.L.-----
FDX 1570 BETWEEN LAYER 4 AND 5AVERAGE SPLIT OFF
STD.DEV.
* 95% C.L.-----
FDX 1572 BETWEEN LAYER 1 AND 2AVERAGE 0.14
STD.DEV. 0.01
* 95% C.L. 0.02-----
FDX 1572 BETWEEN LAYER 4 AND 5AVERAGE 0.06
STD.DEV. 0.00
* 95% C.L. 0.01

=====

OXYGEN TRANSMISSION (OX-TRAN) AT 73 DEG.F., 0% RH

SAMPLE CCSTP/(24HRS,SQ.M.,ATM.) GAUGE, MILS

FDX 15701.9 OPTICAL
1.8
1.6-----
FDX 15723.1 OPTICAL
3.0
2.3-----
PAGES. 142461B-142466B 133082B 142468B *Avi*
40 M H

NOTE1: LAYER GAUGE AND 100% RH OXYGEN TRANSMISSION WILL BE SUBMITTED LATER

NOTE2: COULD ONLY SEPERATE BOND SPECIMEN BETWEEN 2 LAYERS

DATE: 5 15 85

APPROVED BY: *[Signature]** 95% CONFIDENCE LIMITS
FOR THE AVERAGE. N=4

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TSR 1-6777

DETERMINE THE PROPERTIES OF SEVEN LAYER OXYGEN BARRIER SHRINK FILMS

OXYGEN TRANSMISSION (OX-TRAN) AT 73 DEG.F., 100% RH

SAMPLE CCSTP/(24HRS,SQ.M.,ATM.) GAUGE, MILS

FDX 1570

369.3	1.10
346.2	1.28
337.0	1.22

FDX 1572

222.5	1.22
174.5	1.08
152.7	1.31

PAGES: 144516B 145797B *all*
6 M H

NOTE1:

NOTE2:

DATE: 8 9 85

APPROVED BY: *[Signature]*

EXHIBIT 27

EXHIBIT 27

REDACTED IN ITS ENTIRETY

EXHIBIT 28

United States Patent [19]

Yazaki et al.

[11] Patent Number: **4,511,610**[45] Date of Patent: **Apr. 16, 1985**[54] **MULTI-LAYER DRAWN PLASTIC VESSEL**

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[21] Appl. No.: 536,846

[22] Filed: Sep. 29, 1983

[30] Foreign Application Priority Data

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Nov. 2, 1982 [JP] Japan 57-191809

[51] Int. Cl. B65D 85/00; B32B 27/08

[52] U.S. Cl. 428/35; 428/516;
428/910[58] Field of Search 428/516, 517, 518, 519,
428/35, 910

[56] References Cited

FOREIGN PATENT DOCUMENTS63484 6/1978 Japan 428/516
65350 6/1978 Japan 428/516

19718 2/1981 Japan 428/516

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[57] **ABSTRACT**

Disclosed is a multi-layer drawn plastic vessel comprising at least one layer composed mainly of at least one crystalline olefin resin selected from crystalline polypropylene and crystalline propylene/ethylene copolymers having an ethylene content of 1 to 20 mole %, at least one oxygen-barrier layer composed mainly of an ethylene/vinyl alcohol copolymer having an ethylene content of 25 to 60 mole %, and an adhesive resin layer interposed between said two resin layers, said adhesive resin layer containing an acid- or acid anhydride-modified, linear, low-density polyethylene or a mixture of said polyethylene with an acid- or acid anhydride-modified propylene resin and said crystalline olefin resin layer being molecularly oriented in at least one direction.

8 Claims, No Drawings

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MULTI-LAYER DRAWN PLASTIC VESSEL

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to a multi-layer drawn plastic vessel. More particularly, the present invention relates to a multi-layer drawn plastic vessel comprising a laminate having a propylene resin layer and an oxygen-barrier layer formed of an ethylene/vinyl alcohol copolymer, in which the adhesion strength between both the resin layers is prominently improved even though the propylene resin layer is molecularly oriented.

(2) Description of the Prior Art

A laminate formed by bonding a layer of an olefin resin excellent in the moisture resistance, such as polypropylene or polyethylene, to a layer of an ethylene/vinyl alcohol copolymer excellent in the oxygen barrier property through an adhesive layer composed of an acid- or acid anhydride-modified olefin resin is used in various fields as a vessel having an excellent content-preserving quality in the form of a bottle, cup or pouch.

In order to reduce the thickness of the vessel wall as much as possible, improve the rigidity, impact resistance and other mechanical properties of the vessel wall and also improve the transparency and gas barrier property, it is preferred that this multi-layer plastic material be molecularly oriented in at least one direction. Furthermore, plastic processing such as draw forming or biaxial draw-blow forming is advantageous over heat processing because the heat energy cost is low and the productivity is ordinarily high, and by this plastic processing, molecular orientation is naturally caused in the formed vessel wall.

A conventional laminate formed by using an acid- or acid anhydride-modified olefin resin as an adhesive layer has an excellent adhesion strength (peel strength) in the undrawn state, but with increase of the degree of the molecular orientation by drawing, the adhesion strength is gradually reduced and interlaminar peeling is observed in the as-prepared vessel or is readily caused by slight falling shocks. This tendency is especially prominent when polypropylene which is excellent over polyethylene in the rigidity and mechanical strength is used as the olefin resin for outer and inner layers and this polypropylene is oriented by drawing.

Various proposals have heretofore been made in connection with means for controlling reduction of the adhesion strength of a laminate as mentioned above at the draw-forming step. For example, Japanese Patent Publication No. 11585/81 proposes a method in which a blend of an acid- or acid anhydride-modified olefin polymer and a crystalline ethylene copolymer is used as an adhesive layer interposed between the polypropylene layer and the ethylene/vinyl alcohol copolymer layer and a crystalline ethylene copolymer having a melting point lower by 40° to 110° C. than the melting point of the polypropylene is used as the ethylene copolymer contained in the blend. According to this proposal, the interlaminar peeling resistance is improved, but if the polypropylene layer is highly molecularly oriented, it is impossible to prevent the interlaminar peeling completely.

SUMMARY OF THE INVENTION

It is therefore a primary object of the present invention to provide a multi-layer drawn plastic vessel com-

prising a layer composed of at least one member selected from crystalline polypropylene and crystalline propylene/ethylene copolymers, a layer composed of an ethylene/vinyl alcohol copolymer, said two layers being bonded to each other through a layer containing an acid- or acid anhydride-modified, linear, low-density polyethylene, in which the interlaminar peeling resistance is highly improved and the degree of molecular orientation of the vessel wall is increased.

Another object of the present invention is to provide a multi-layer drawn plastic vessel comprising a layer composed of at least one member selected from crystalline polypropylene and crystalline propylene/ethylene copolymers and a layer composed of an ethylene/vinyl alcohol copolymer, said two layers being bonded to each other through an adhesive layer composed of an acid- or acid anhydride-modified olefin resin composition, in which the drawing temperature for the propylene resin layer is matched with the melting characteristics of the adhesive layer, whereby the interlaminar peeling resistance is highly improved and the degree of molecular orientation of the vessel wall is increased.

Still another object of the present invention is to provide a multi-layer drawn plastic vessel which comprises constituent resin layers excellent in the interlaminar peeling resistance though the vessel is prepared through plastic processing such as biaxial draw-blow forming or draw processing.

A further object of the present invention is to provide a biaxially drawn, blow-molded vessel.

A still further object of the present invention is to provide a seamless plastic vessel prepared by draw forming.

A still further object of the present invention is to provide a multi-layer drawn plastic vessel which is excellent in the adaptability to the forming operation and the productivity.

In accordance with one fundamental aspect of the present invention, there is provided a multi-layer drawn plastic vessel comprising at least one layer composed mainly of at least one crystalline olefin resin selected from crystalline polypropylene and crystalline propylene/ethylene copolymers having an ethylene content of 1 to 20 mole %, at least one oxygen-barrier layer composed mainly of an ethylene/vinyl alcohol copolymer having an ethylene content of 25 to 60 mole %, and an adhesive resin layer interposed between said two resin layers, said adhesive resin layer containing an acid- or acid anhydride-modified, linear, low-density polyethylene and said crystalline olefin resin layer being molecularly oriented in at least one direction.

In accordance with one preferred embodiment of the present invention, there is provided a multi-layer drawn plastic vessel comprising at least one layer composed mainly of at least one crystalline olefin resin selected from crystalline polypropylene and crystalline propylene/ethylene copolymers having an ethylene content of 1 to 20 mole %, at least one oxygen-barrier layer composed mainly of an ethylene/vinyl alcohol copolymer having an ethylene content of 25 to 60 mole %, and an adhesive layer interposed between said two resin layers, said adhesive layer being composed of a composition comprising an acid- or acid anhydride-modified, linear, low-density polyethylene and an acid- or acid anhydride-modified propylene resin at a weight ratio of from 95/5 to 50/50 and said crystalline olefin

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resin layer being molecularly oriented in at least one direction.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is characterized in that among various acid- and acid anhydride-modified olefin resins, an acid- or acid anhydride-modified resin based on linear low-density polyethylene or a resin composition comprising this modified resin and an acid- or acid anhydride-modified propylene resin is especially selected and is used as the adhesive resin layer.

Linear low-density polyethylene used as the base of the acid- or acid anhydride-modified resin has several characteristics not possessed by ordinary high-pressure method low-density polyethylene or low-pressure method high-density polyethylene.

For example, although high-pressure method low-density polyethylene is a homopolymer of ethylene having a molecular structure having long-chain branches, linear low-density polyethylene has a substantially linear molecular structure and consists of a copolymer of ethylene with an α -olefin having 4 to 8 carbon atoms. On the other hand, low-pressure method high density polyethylene has a density of 0.940 to 0.965 g/cm³ (as measured at 25° C.) and its molecular structure is substantially free of short branches, but linear low-density polyethylene has a density of 0.915 to 0.935 g/cm³ and its molecular structure has short branches derived from the above-mentioned α -olefin.

As the comonomer in this linear low-density polyethylene, there can be mentioned α -olefins having 4 to 8 carbon atoms, such as butene-1, pentene-1, 4-methylpentene-1, hexene-1, 2-methylbutene-1 and octene-1. The α -olefin is included in the polymer chain in an amount of 1 to 20 % by weight, especially 3 to 15% by weight, based on the total polymer.

Because of the above-mentioned differences of the chemical structure, linear low-density polyethylene (L-LDPE) has physical properties different from those of other olefin resins such as high-pressure method low-density polyethylene (HP-LDPE), high-density polyethylene (HDPE) and a crystalline propylene/ethylene copolymer (PPE), as shown in Table A given below.

TABLE A

Resin	Elongation (%)	Strength (Kg/cm ²)	Melting Point (°C)
L-LDPE	550	300	106-122
HP-LDPE	600	120	94-114
HDPE	800	230	118-133
PPE	800	330	125-153

From the data shown in Table A, it will readily be understood that linear low density polyethylene to be used as the base of the modified resin has a low melting point while it has high elongation and strength.

The modified resin used in the present invention is easily obtained by graft-modifying the above-mentioned linear low-density polyethylene with an ethylenically unsaturated carboxylic acid or an anhydride thereof. As the ethylenically unsaturated carboxylic acid or its anhydride, there can be mentioned maleic anhydride, maleic acid, fumaric acid, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, citraconic acid and hexahydrophthalic anhydride. Carbonyl groups



derived from the acid or acid anhydride, can be contained at a concentration of 1 to 600 milliequivalents, especially 5 to 400 milliequivalents, per 100 g of the polymer based on the final resin.

It is ordinarily preferred that the modified polyethylene should have a melting point of 115° to 135° C.

The adhesive layer used in the present invention may be composed of an acid-modified linear low-density polyethylene alone or a blend of an acid-modified linear low-density polyethylene and an unmodified linear low-density polyethylene. In the latter case, the blending ratio of both the resins may optionally be changed, so far as the carbonyl group concentration in the blend is within the above-mentioned range. Moreover, this adhesive layer may be composed of a blend of linear low-density polyethylene and other olefin resin such as acid-modified or unmodified crystalline polypropylene, high-density polyethylene, high-pressure method low-density polyethylene or a crystalline ethylene/propylene copolymer, so far as the linear low-density polyethylene content is at least 50% by weight and the carbonyl group concentration in the blend is within the above-mentioned range.

According to the present invention, by using the adhesive layer composed mainly of an acid- or acid anhydride-modified linear low-density polyethylene, even if a laminate structure comprising a polypropylene layer and an ethylene/vinyl alcohol copolymer layer is highly drawn, the peel strength of the laminate is highly improved. Ordinarily, when a laminate of this type is drawn, peeling is not caused between the propylene resin layer and the adhesive resin layer but peeling is caused between the adhesive layer and the ethylene/vinyl alcohol copolymer layer. Table B given below shows data of the peel strength (Kg/15 mm width) obtained when a laminate sheet of a maleic anhydride-modified olefin resin having a carbonyl group concentration of 94 milliequivalents (meq) per 100 g of the polymer and an ethylene/vinyl alcohol copolymer having an ethylene content of 40 mole % was drawn at 150° C. at various draw ratios.

TABLE B

Base of Modified Resin	Draw Ratio			
	0	3	5	10
L-LDPE	above 4	1	1	0.4
HP-LDPE	above 4	0.3	0-0.02	0-0.02
HDPE	above 4	1	0.4	0.05
PPE	above 4	0.5	0-0.02	0-0.02

From the data shown in Table B, it will readily be understood that in the case where any acid-modified olefin resin is used, a high adhesion strength is obtained in the undrawn state, but if the draw ratio is increased, the adhesion strength is drastically reduced but when an acid-modified resin derived from L-LDPE as the base is used, an excellent adhesion strength is obtained within a practical draw ratio range.

The reasons why, an excellent interlaminar adhesion strength can be obtained even at a high draw ratio when an acid- or acid anhydride-modified linear low-density polyethylene is used as the adhesive resin layer accord-

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ing to the present invention are considered to be as follows.

This specific adhesive resin layer is present in the molten state under the propylene-drawing conditions and has such a property that this melt is well elongated even under a relatively low tension.

Table C shows data of the elongation and tension obtained at 160° C. with reference to melts of acid-modified resins derived from various olefin resin bases.

TABLE C

Base Resin	Elongation (%)	Tension (g)
L-LDPE	240	8.7
HP-LDPE	60	15.8
HDPE	150	10.3
PPE	200	11.5

From the data shown in Table C, it will readily be understood that the modified resin based on linear low-density polyethylene has such a property that the resin is well elongated in the molten state under a relatively low tension, and it is considered that by dint of this characteristic property, in the laminated vessel of the present invention, the fracture of the bonded interface at the draw-forming step or the presence of the residual strain in the bonded interface is prevented and an excellent adhesion strength is maintained even at a high draw ratio. Moreover, it is believed that the fact that this adhesive resin per se has an excellent mechanical strength in the normal state is contributory to the increase of the adhesion strength. Incidentally, it must be noted that the physical properties are not substantially changed by the acid modification included within the above-mentioned range.

The acid- or acid anhydride-modified linear low-density polyethylene used in the present invention has a low melt tension in the range of from 5 to 9 g as measured at 170° C. by a melt tension tester (nozzle length L=8 mm, nozzle diameter=2.1 mm, extrusion speed=10 mm/min).

In accordance with one preferred embodiment of the present invention, there is provided a resin composition comprising (A) an acid-modified, linear, low-density polyethylene and (B) an acid-modified propylene resin at an (A)/(B) weight ratio of from 95/5 to 50/50, especially from 90/10 to 60/40.

As is apparent from the data shown in Table B given hereinbefore, the acid-modified linear low density polyethylene is advantageous in that it gives a high interlaminar adhesion strength even at a high draw ratio, but under high draw ratio conditions adopted for drawing crystalline propylene or a crystalline propylene/ethylene copolymer, a thick portion and a thin portion are formed in the adhesive layer of this acid-modified linear low-density polyethylene and the thickness becomes uneven, and fusion fracture of the adhesive layer is caused in an extreme case and a portion having a very small adhesive force is locally formed in the drawn structure.

From the results of researches made by us, it is construed that since the linear low-density polyethylene has a low melting point among various olefin resins and it has a considerably small melt tension, flowing or fusion fracture rendering the thickness uneven is readily caused under the conditions for drawing the crystalline propylene resin layer.

As shown in Table C given hereinbefore, the acid-modified linear low-density polyethylene has a small

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melt tension. This defect results in the following disadvantage. Namely, at the step of preparing a pipe-like multi-layer parison or preform by extrusion or at the step of preheating the parison or preform for the drawing operation, it sometimes happens that the inner layer portion is thrown clear from the outer layer portion of the parison and the adaptability to the forming operation is considerably reduced.

According to the above-mentioned preferred embodiment of the present invention, by incorporating an acid-modified propylene resin into this acid-modified linear low-density polyethylene, non-uniformization of the thickness (thickness unevenness) of the adhesive layer under drawing conditions or fusion fracture of the adhesive layer can be prevented while maintaining a high interlaminar adhesion strength even at a high draw ratio, and reduction of the operation adaptability due to a low melt tension is moderated.

In this preferred embodiment of the present invention, if the amount incorporated of the acid-modified propylene resin is too large and exceeds the above range, reduction of the adhesive force under drawing conditions tends to be prominent, and if the amount of the acid-modified propylene resin is too small and below the above range, troubles are caused because of the unevenness of the adhesive layer.

The reason why the acid-modified propylene resin used as the other modified resin component exerts the above-mentioned function has not been elucidated. However, it is believed that since the acid-modified propylene resin has an excellent compatibility with the acid-modified linear low density polyethylene and inhibits melt flowing of the acid-modified linear low-density polyethylene, the acid-modified propylene resin will probably exert the above function.

The acid-modified propylene resin to be used in the present invention is prepared by modifying crystalline polypropylene or a crystalline propylene/ethylene copolymer having an ethylene content of 1 to 20 mole % with an ethylenically unsaturated carboxylic acid or an anhydride thereof as in case of the linear low-density polyethylene, and the acid-modified propylene resin contains carbonyl groups derived from the acid or anhydride at a concentration of 1 to 600 meq/100 g of the polymer, especially 5 to 400 meq/100 g of the polymer.

It is preferred that the melting point of the modified propylene resin be 148° to 167° C., especially lower than the temperature adopted for drawing the multi-layer structure, though the preferred melting point varies to some extent according to the ethylene content.

In view of the rigidity, mechanical strength and transparency, it is important that crystalline polypropylene or a crystalline propylene/ethylene copolymer having an ethylene content of 1 to 20 mole % should be used as the olefin resin layer in the multi-layer vessel of the present invention. In the present invention, even if this crystalline polypropylene or propylene/ethylene copolymer is used, an excellent interlaminar peeling resistance can be attained. This is one of advantages attained by the present invention.

A layer comprising the above-mentioned crystalline polypropylene or propylene/ethylene copolymer and a small amount of the resin constituting the oxygen barrier layer or adhesive layer may be used as the layer composed mainly of the olefin resin. Accordingly, burrs or fins formed at the blow molding step may be used as the olefin resin layer or a part thereof.

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In view of the oxygen-barrier property, a copolymer obtained by saponifying an ethylene/vinyl acetate copolymer having an ethylene content of 25 to 60 mole % to a saponification degree of at least 96%, especially at least 99%, is preferably used as the ethylene/vinyl alcohol copolymer in the multi-layer vessel of the present invention. Of course, other thermoplastic resin may be incorporated in the oxygen-barrier layer, so far as the characteristic properties of the ethylene/vinyl alcohol copolymer are not impaired.

In the present invention, an optional layer arrangement can be adopted, so far as the adhesive layer (C) is interposed between the oxygen-barrier layer (A) and the olefin resin layer (B). For example, the following layer arrangements may be adopted.

- (1) Three-layer structure of (A)/(C)/(B).
- (2) Four-layer structure of (C)/(A)/(C)/(B).
- (3) Five-layer structures of (B)/(C)/(A)/(C)/(B), (B)/(C)/(A)/(C)/(B) and (B+A+C)/(C)/(A)/(C)/(B+A+C).
- (4) Six-layer structures of (B)/(B)/(C)/(A)/(C)/(B) and (B)/(B+A+C)/(C)/(A)/(C)/(B).
- (5) Seven-layer structures of (B)/(B+A+C)/(C)/(A)/(C)/(B+A+C)/(B) and (B)/(B)/(C)/(A)/(C)/(B)/(B).

The thickness of each layer is not particularly critical in the multi-layer vessel. However, it is ordinarily preferred that the (B)/(A) thickness ratio be in the range of from 1/1 to 500/1 and the (B)/(C) thickness ratio be in the range of from 1/1 to 500/1.

According to the present invention, a parison or sheet having the above-mentioned multi-layer structure is formed by co-melt extrusion, and this parison or sheet is formed into a vessel by known plastic forming means.

A multi-layer parison is prepared by co-melt extrusion or simultaneous injection molding of the above-mentioned resin layers, and a biaxially drawn blow-molded vessel can be obtained by drawing this parison in the axial direction and simultaneously or sequentially inflating the parison in the transverse direction by a fluid.

A multi-layer sheet is obtained by forming the above-mentioned resin layers into a sheet according to the T-die method, the inflation method or the like, and a seamless cup-shaped drawn vessel can be obtained by molding this sheet by plug-assist forming, draw forming using a die and punch, air-pressure forming draw-iron forming.

In the present invention, in order to improve the rigidity, mechanical strength and transparency of the vessel, it is important that the olefin resin layer should be oriented by drawing. This orientation can easily be accomplished by carrying out biaxial draw-blow forming of the parison or draw forming of the sheet at a temperature just below the melting point of the olefin resin or slightly lower than the melting point of the olefin resin. In the present invention, if the above-mentioned adhesive layer (C) is used, forming can be performed at a temperature higher than the melting point of the adhesive layer while imparting effective orientation to the olefin resin layer, and therefore, it becomes possible to improve the interlaminar peeling resistance between the respective resin layers and the impact resistance while highly improving the rigidity, mechanical strength, gas barrier property and transparency of the vessel.

In the present invention, if draw forming is carried out under the above-mentioned conditions, a multi-

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layer drawn vessel having highly improved transparency, rigidity and gas barrier property and an especially high interlaminar peeling resistance can be obtained. Furthermore, by this drawing operation, the thickness of the vessel can be reduced, the weight can be reduced and the amount used of the resins can be decreased. In case of a biaxially drawn and blown vessel, the draw ratio can be 1.5 to 5 in the axial direction and 2 to 10 in the circumferential direction, and biaxial molecular orientation can be given to the vessel. In case of a drawn vessel such as a cup, the contraction ratio, that is, the ratio of the vessel height to the mouth diameter, can be 0.2 to 5, and molecular orientation is given in the axial direction.

In the formed vessel of the present invention, the basis weight (the volume per g of the resin) is ordinarily 0.01 to 5 dl/g and especially 0.05 to 2 dl/g, though the basis weight varies to some extent according to the intended use. The thickness of the vessel wall is ordinarily 0.02 to 1 mm and especially 0.08 to 0.8 mm. If the basis weight and thickness are arranged within these ranges, a desirable combination of the gas barrier property, rigidity and transparency can be attained.

The vessel of the present invention is valuable as a vessel for preserving the content as it is or after it has been subjected to such a treatment as hot filling or heat sterilization. Namely, the vessel of the present invention is valuable as a vessel for preserving with much reduced deterioration or weight decrease liquid or pasty foods or drinks, for example, alcoholic drinks such as carbonated alcoholic drinks, e.g., beer, Japanese sake, whisky, low-class distilled spirits, ratafia, e.g., wine and cocktails, e.g., gin fizz, carbonated drinks such as cola, cider and plain soda, straight juices such as lemon juice, orange juice, plum juice, grape juice and strawberry juice, fruit juice-containing processed drinks such as Nector juice, vegetable drinks such as tomato juice and other vegetable juices, synthetic drinks or vitamin-added drinks such as synthetic fruit juices comprising saccharide such as sugar or fructose, citric acid, a colorant and a perfume, optionally with vitamins, lactic acid beverages, stews such as cooked curry, cooked hash, borsch and beef stew, gravies such as meat sauce, boiled vegetables, fishes and meats such as sweet-and-sour port, sukiyaki, Chinese hoosh and hotchpotch, boiled asparagus, boiled beans and cream-boiled tuna, soups such as consomme, potage, miso soup, pork-mixed miso soup and chowder, rice foods such as boiled rice, cooked rice with red beans, fried rice, pilaf and rice gruel, noodles such as spaghetti, buckwheat vermicelli, wheat vermicelli, Chinese noodles and macaroni, composite seasonings for fried rice soups or Chinese noodle soups, table luxuries such as boiled red beans, boiled peas with honey and bean jam, custard pudding, jelly and soft bean jelly, processed marine products and livestock products such as meat dumpling, hamburger, corned beef, sausage, roast fish, smoked fish, bacon and boiled fish paste, fruits such as orange, pineapple, peach, cherry and olive, seasonings such as soy sauce, sauce, vinegar, dressing, mayonnaise and ketchup, and other subsidiary foods such as bean curd, jam, butter and margarin; medicines such as Ringer's solution, agricultural chemicals, cosmetics and detergents; ketones such as acetone and methylethyl ketone, aliphatic hydrocarbons such as n-hexane and n-heptane, alicyclic hydrocarbons such as cyclohexane, aromatic hydrocarbons benzene, toluene and xylene; chlorine-containing compounds such as carbon tetrachloride, tetrachloroethane

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and tetrachloroethylene, high fatty acids; gasolin, kerosene, petroleum, benzene, heavy oil, thinner, grease, silicon oil, light oil and machine oil; and liquefied Freon (the tradename for the product supplied by Ro Pont).

The present invention will now be described in detail with reference to the following Examples that by no means limit the scope of the invention.

EXAMPLE 1

For the production of a bottle having a five-layer structure of outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer, a bottomless multi-layer pipe having a five-layer structure was formed by using an extruder having a diameter of 40 mm, an effective length of 880 mm and one melt channel (for the intermediate layer), an extruder having a diameter of 40 mm, an effective length of 880 mm and two melt channels (for the adhesive layers), an extruder having a diameter of 65 mm, an effective length of 1430 mm and two melt channels (for the inner and outer layers), and a co-extrusion 5-ply die. An ethylene/propylene copolymer having a melt index of 2.0 g/10 min, a density of 0.89 g/cc and a melting point of 158° C. as determined by the DTA method (the temperature elevation rate was 10° C./min) was used as the inner and outer layers. An ethylene/vinyl alcohol copolymer having an ethylene content of 42 mole %, a vinyl alcohol content of 58 mole % and a melting point of 163° C. as determined according to the above-mentioned method was used as the oxygen-barrier layer (intermediate layer). As the adhesive layer resin, there was used (1) a modified linear low-density polyethylene having a melt index of 0.4 g/10 min, a density of 0.93 g/cc, a melting point of 122° C. as determined by the above-mentioned method and a carbonyl group concentration of 94 meq/100 g of the polymer or (2) a mixture comprising the above-mentioned modified linear low-density polyethylene and an unmodified linear low-density polyethylene at a weight ratio of 90/10.

The outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer thickness ratio in the formed pipe was 1:1/200:1/5:1/200:1.

The entire thickness of the pipe was about 10 mm, and the inner diameter was 30 mm and the length was 30 mm. The pipe formed by using the adhesive resin (1) is designated as "pipe A" and the pipe formed by using the adhesive resin (2) is designated as "pipe B".

Each pipe was heated for 25 minutes in an atmosphere maintained at $134 \pm 1^\circ \text{C}$, and the pipe was drawn in the longitudinal direction at a draw ratio of about 3 by pinching both the ends of the pipe by clamps, and the drawn pipe was inserted in a blowing mold and air was blown into the so-formed parison from one end thereof to inflate the parison in the transverse direction and effect blow forming. Thus, biaxially drawn blow-flowed bottles AB and BB having the above-mentioned 5-layer structure were obtained. Each bottle had an inner diameter of 100 mm and a height of 150 mm, and the average wall thickness was 0.6 mm, the inner capacity was about 1000 cc and the basis weight was about 0.31 dl/g. Each bottle had a cylindrical shape.

With respect to each bottle, the oxygen permeability (QO_2) was measured according to the method disclosed in Japanese Patent Publication No. 11263/77 and the haze (Hz) was measured according to the method of JIS K-6714. Twenty samples each of the bottles AB and BB were filled with 1000 cc of water and they were let to fall down on a concrete floor from a height of 120 cm at

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normal temperature. The presence or absence of interlaminar peeling in the bottom, bottom corner, barrel and mouth was visually checked by a panel of 5 experts to evaluate the interlaminar peeling resistance.

For comparison, a bottle CB was prepared in the same manner as described above except that low density polyethylene having a carbonyl group concentration of 94 meq/100 g of the polymer and a melting point of 110° C. was used as the adhesive resin.

The results of evaluation of these bottles are shown in Table 1. The bottles AB, BB and CB were not substantially different from one another in the oxygen permeability, but the bottles AB and BB were excellent over the bottle CB in the haze and interlaminar peeling resistance.

TABLE 1

Bottle	Oxygen Permeability ($\text{cc}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$)	Haze (%)	Interlaminar Peeling (%)
AB	4.2	10.8	0.0
BB	4.1	10.2	1.0
CB	4.3	17.6	75.0

EXAMPLE 2

A 5-layer sheet (0.8 mm in thickness) in which the outer layer/adhesive layer/oxygen-barrier layer (intermediate layer)/adhesive layer/inner layer thickness ratio was 1:1/50:1/20:1/50:1 was formed by using a 5-ply T-die and a sheet forming machine. An isotactic propylene homopolymer having a melt index of 0.5 g/10 min (as measured according to the method of ASTM D-1238; the same will apply hereinafter), a density of 0.91 g/cc (as measured according to the method of ASTM D-1505; the same will apply hereinafter) and a melting point of 165° C. as determined according to the DTA method (the temperature elevation rate was 10° C./min) was used as the inner and outer layers, an ethylene/vinyl alcohol copolymer having an ethylene content of 30 mole %, a vinyl alcohol content of 70 mole % and a melting point of 183° C. was used as the oxygen-barrier layer (hereinafter referred to as "intermediate layer"), and a modified linear low-density polyethylene having a melt index of 2.0 g/10 min, a density of 0.93 g/cc, a melting point of 122° C. and a carbonyl group concentration of 94 meq/100 g of the polymer was used as the adhesive layer resin. This laminated sheet was uniformly heated at 162° C. and was formed into an angular cup (cup DC) having a length of 140 mm, a width of 100 mm, a height of 40 mm, a side wall thickness of 0.4 mm and an inner capacity of 500 cc according to the known plug-assist air-pressure forming method.

For comparison, a laminated cup (cup EC) was prepared in the same manner as described above except that a modified propylene polymer having a melting point of 163° C. and a carbonyl group concentration of 48 meq/100 g of the polymer was used as the adhesive layer resin.

These cups were evaluated in the same manner as described in Example 1. The obtained results are shown in Table 2.

TABLE 2

Cup	Oxygen Permeability ($\text{cc}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$)	Haze (%)	Interlaminar Peeling (%)
DC	7.8	9.8	0.0
EC	7.9	10.7	5.0 (corner)

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TABLE 2-continued

Cup	Oxygen Permeability (cc/m ² · day · atm)	Haze (%)	Interlaminar Peeling (%) portions)
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EXAMPLE 3

For the production of a bottle having a five-layer structure of outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer, a bottomless multi-layer pipe having a five-layer structure was formed by using an extruder having a diameter of 40 mm, an effective length of 880 mm and one melt channel (for the intermediate layer), an extruder having a diameter of 40 mm, an effective length of 880 mm and two melt channels (for the adhesive layers), an extruder having a diameter of 65 mm, an effective length of 1430 mm and two melt channels (for the inner and outer layers), and a co-extrusion 5-ply die. An ethylene/propylene copolymer having a melt index of 2.0 g/10 min, a density of 0.89 g/cc and a melting point of 158° C. as determined by the DTA method (the temperature elevation rate was 10° C/min) was used as the inner and outer layers. An ethylene/vinyl alcohol copolymer having an ethylene content of 42 mole %, a vinyl alcohol content of 58 mole % and a melting point of 163° C. as determined according to the above-mentioned method was used as the oxygen-barrier layer (intermediate layer). As the adhesive layer resin, there was used a mixture comprising 80 parts by weight of a modified linear low-density polyethylene having a melt index of 0.4 g/10 min, a density of 0.93 g/cc, a melting point of 122° C. as determined by the above-mentioned method and a carbonyl group concentration of 94 meq/100 g of the polymer and 20 parts by weight of a modified ethylene/propylene copolymer having an ethylene content of 3 mole %, a melting point of 155° C. and a carbonyl group concentration of 65 meq/100 g of the polymer.

The outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer thickness ratio in the formed pipe was 1:1/200:1/5:1/200:1.

The entire thickness of the pipe was about 6 mm, and the inner diameter was 30 mm and the length was 30 mm.

The pipe was heated for 25 minutes in an atmosphere maintained at 154±1° C., and the pipe was drawn in the longitudinal direction at a draw ratio of about 3 by pinching both the ends of the pipe by clamps, and the drawn pipe was inserted in a blowing mold and air was blown into the so-formed parison from one end thereof to inflate the parison in the transverse direction and effect blow forming. Thus, a biaxially drawn blow-formed bottle having the above-mentioned 5-layer structure was obtained. The bottle had an inner diameter of 100 mm and a height of 150 mm, and the average wall thickness was 0.6 mm, the inner capacity was about 1000 cc and the basis weight was about 0.31 dl/g. The bottle had a cylindrical shape.

With respect to the so-obtained bottle, the oxygen permeability (QO₂) was measured according to the method disclosed in Japanese Patent Publication No.11263/77 and the haze (Hz) was measured according to the method of JIS K-6714. Twenty samples of the bottle were filled with 1000 cc of water and they were let to fall down on a concrete floor from a height of 120 cm at normal temperature. The presence of absence of interlaminar peeling in the bottom, bottom corner, bar-

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rel and mouth was visually checked by a panel of 5 experts to evaluate the interlaminar peeling resistance.

For comparison, a bottle was prepared in the same manner as described above except that a modified ethylene/propylene copolymer having a carbonyl group concentration of 94 meq/100 g of the polymer and a melting point of 155° C. was used as the adhesive resin.

The results of evaluation of these bottles are shown in Table 3. The bottles were not substantially different from each other in the oxygen permeability, but the bottle to the present invention was excellent over the comparative bottle in the haze and interlaminar peeling resistance.

TABLE 3

Bottle	Oxygen Permeability (cc/m ² · day · atm)	Haze (%)	Interlaminar Peeling (%)
present invention	7.2	1.3	0.0
comparison	7.3	13.0	100

EXAMPLE 4

A 5-layer sheet (1.2 mm in thickness) in which the outer layer/adhesive layer/oxygen-barrier layer (intermediate layer)/adhesive layer/inner layer thickness ratio was 1:1/50:1/20:1/50:1 was formed by using a 5-ply T-die and a sheet forming machine. An isotactic propylene homopolymer having a melt index of 0.5 g/10 min (as measured according to the method of ASTM D-1238; the same will apply hereinafter), a density of 0.91 g/cc (as measured according to the method of ASTM D-1505; the same will apply hereinafter) and a melting point of 165° C. as determined according to the DTA method (the temperature elevation rate was 10° C/min) was used as the inner and outer layers, an ethylene/vinyl alcohol copolymer having an ethylene content of 30 mole %, a vinyl alcohol content of 70 mole % and a melting point of 183° C. was used as the oxygen-barrier layer (hereinafter referred to as "intermediate layer"), and a mixture comprising 60 parts by weight of a modified linear low-density polyethylene having a melt index of 2.0 g/10 min, a density of 0.93 g/cc, a melting point of 122° C. and a carbonyl group concentration of 94 meq/100 g of the polymer and 40 parts by weight of a modified ethylene/propylene copolymer having an ethylene content of 2 mole %, a melting point of 157° C. and a carbonyl group concentration of 70 meq/100 g of the polymer was used as the adhesive layer resin. This laminated sheet was uniformly heated at 160° C. and was formed into an angular cup having a length of 70 mm, a width of 70 mm, a height of 100 mm, a side wall thickness of 0.4 mm and an inner capacity of 500 cc according to the known plug-assist air-pressure forming method.

For comparison, a laminated cup was prepared in the same manner as described above except that a modified propylene polymer having a melting point of 157° C. and a carbonyl group concentration of 70 meq/100 g of the polymer was used as the adhesive layer resin.

These cups were evaluated in the same manner as described in Example 3. The obtained results are shown in Table 4.

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TABLE 4

Cup	Oxygen Permeability (cc/m ² · day · atm)	Haze (%)	Interlaminar Peeling (%)
present	7.8	9.8	0.0
invention			
comparison	7.9	10.7	33.0 (corner portions)

EXAMPLE 5

For the production of a bottle having a five-layer structure of outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer, a bottomless multi-layer pipe having a five-layer structure was formed by using an extruder having a diameter of 40 mm, an effective length of 880 mm and one melt channel (for the intermediate layer), an extruder having a diameter of 40 mm, an effective length of 880 mm and two melt channels (for the adhesive layers), an extruder having a diameter of 65 mm, an effective length of 1430 mm and two melt channels (for the inner and outer layers), and a co-extrusion 5-ply die. An ethylene/propylene copolymer having a melt index of 2.0 g/10 min, a density of 0.89 g/cc and a melting point of 158° C. as determined by the DTA method (the temperature elevation rate was 10° C./min) was used as the inner and outer layers. An ethylene/vinyl alcohol copolymer having an ethylene content of 42 mole %, a vinyl alcohol content of 58 mole % and a melting point of 163° C. as determined according to the above-mentioned method was used as the oxygen-barrier layer (intermediate layer). As the adhesive layer resin, there was used (1) a modified linear low-density polyethylene having a melt index of 0.3 g/10 min, a density of 0.93 g/cc, a melting point of 122° C. as determined by the above-mentioned method and a carbonyl group concentration of 5 meq/100 g of the polymer or (2) a mixture comprising the above-mentioned modified linear low-density polyethylene and an unmodified linear low-density polyethylene at a weight ratio of 90/10.

The outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer thickness ratio in the formed pipe was 1:1/200:1/3:1/200:1.

The entire thickness of the pipe was about 10 mm, and the inner diameter was 30 mm and the length was 30 mm. The pipe formed by using the adhesive resin (1) is designated as "pipe F" and the pipe formed by using the adhesive resin (2) is designated as "pipe G".

Each pipe was heated for 25 minutes in an atmosphere maintained at 154±1° C., and the pipe was drawn in the longitudinal direction at a draw ratio of about 3 by pinching both the ends of the pipe by clamps, and the drawn pipe was inserted in a blowing mold and air was blown into the so-formed parison from one end thereof to inflate the parison in the transverse direction and effect blow forming. Thus, biaxially drawn blow-formed bottles FB and GB having the above-mentioned 5-layer structure were obtained. Each bottle had an inner diameter of 100 mm and a height of 150 mm, and the average wall thickness was 0.6 mm, the inner capacity was about 1000 cc and the basis weight was about 0.31 dl/g. Each bottle had a cylindrical shape.

With respect to each bottle, the oxygen permeability (O₂) was measured according to the method disclosed in Japanese Patent Publication No. 11263/77 and the haze (Hz) was measured according to the method of JIS K-6714. Twenty samples each of the bottles FB and GB were filled with 1000 cc of water and they were let to

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fall down on a concrete floor from a height of 120 cm at normal temperature. The presence or absence of interlaminar peeling in the bottom, bottom corner, barrel and mouth was visually checked by a panel of 5 experts to evaluate the interlaminar peeling resistance.

For comparison, a bottle HB was prepared in the same manner as described above except that low density polyethylene having a carbonyl group concentration of 5 meq/100 g of the polymer and a melting point of 110° C. was used as the adhesive resin.

The results of evaluation of these bottles are shown in Table 1. The bottles FB, GB and HB were not substantially different from one another in the oxygen permeability, but the bottles FB and GB were excellent over the bottle HB in the haze and interlaminar peeling resistance.

TABLE 5

Bottle	Oxygen Permeability (cc/m ² · day · atm)	Haze (%)	Interlaminar Peeling (%)
FB	4.2	9.5	2.0
GB	4.1	9.7	3.0
HB	4.3	16.8	100

What is claimed is:

1. A multi-layer drawn plastic vessel comprising at least one layer comprising at least one crystalline olefin resin selected from the group consisting of crystalline polypropylene and crystalline propylene/ethylene copolymers having an ethylene content of 1 to 20 mole %, at least one oxygen-barrier layer comprising an ethylene/vinyl alcohol copolymer having an ethylene content of 25 to 60 mole %, and an adhesive resin layer interposed between said two resin layers, said adhesive resin layer comprising an acid- or acid anhydride-modified, linear, low-density polyethylene and said crystalline olefin resin layer being molecularly oriented in at least one direction.

2. A vessel as set forth in claim 1, wherein the adhesive resin layer contains carbonyl groups derived from the acid or acid anhydride at a concentration of 1 to 600 meq/100 g of the polymer.

3. A vessel as set forth in claim 1, wherein the acid- or acid anhydride-modified, linear, low-density polyethylene has a density of 0.915 to 0.935 g/cm³ and a melt tension of 5 to 9 g as measured at 170° C.

4. A vessel as set forth in claim 1, wherein the acid- or acid anhydride-modified, linear, low-density polyethylene has a melting point of 115° to 135° C.

5. A multi-layer drawn plastic vessel comprising at least one layer comprising at least one crystalline olefin resin selected from the group consisting of crystalline polypropylene and crystalline propylene/ethylene copolymers having an ethylene content of 1 to 20 mole %, at least one oxygen-barrier layer comprising an ethylene/vinyl alcohol copolymer having an ethylene content of 25 to 60 mole %, and an adhesive layer interposed between said two resin layers, said adhesive layer comprising an acid- or acid anhydride-modified, linear, low-density polyethylene and an acid- or acid anhydride-modified propylene resin at a weight ratio of from 95/5 to 50/50 and said crystalline olefin resin layer being molecularly oriented in at least one direction.

6. A vessel as set forth in claim 5, wherein the weight ratio of the acid- or acid anhydride-modified, linear, low-density polyethylene to the acid- or acid anhydride-modified propylene is in the range of from 90/10 to 60/40.

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7. A vessel as set forth in claim 5, wherein the acid- or acid anhydride-modified propylene resin contains carbonyl groups derived from the acid or acid anhydride at a concentration of 1 to 600 meq/100 g of the polymer.

acid anhydride-modified propylene resin has a melting point of 148° to 167° C.

8. A vessel as set forth in claim 5, wherein the acid- or

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EXHIBIT 29

United States Patent [19]**Dallmann et al.**[11] **Patent Number:** **4,572,854**[45] **Date of Patent:** **Feb. 25, 1986**

[54] **MULTILAYER FILM WITH A GAS AND AROMA BARRIER LAYER AND A PROCESS FOR THE PREPARATION AND APPLICATION THEREOF**

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[52] **U.S. Cl.** 428/35; 428/349;
428/516; 428/518; 428/520; 156/244.11
[58] **Field of Search** 428/516, 349, 35, 518,
428/520, 522; 156/244.11

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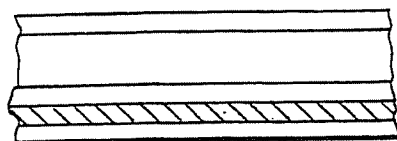
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Mack, Blumenthal & Evans

[57] **ABSTRACT**

The invention concerns a multilayer, preferably sealable film, comprising one or more inner layers; more specifically, (1) an inner barrier layer D containing a saponified ethylene-vinyl acetate polymer having 15 to 60 mole % ethylene units and being saponified to at least 90 mole %; and (2) at least one layer immediately adjacent to the surface of the barrier layer D, which layer is an adhesion-promoting layer C and comprises a modified polymer or the modified polyolefin. All layers of the film are oriented at least biaxially under identical conditions. On one side of the barrier layer D, adjacent to the first adhesion-promoting layer C, a first layer B is located, and an optionally, a sealable layer A, is adjacent thereto. Layer B contains a polypropylene homopolymer and/or a propylene copolymer and/or the material of the layer C and/or the material of the optional layer A. Also disclosed is a process for the preparation of a multilayer film as described, and its use, in particular, in the packaging of oxygen-sensitive goods.

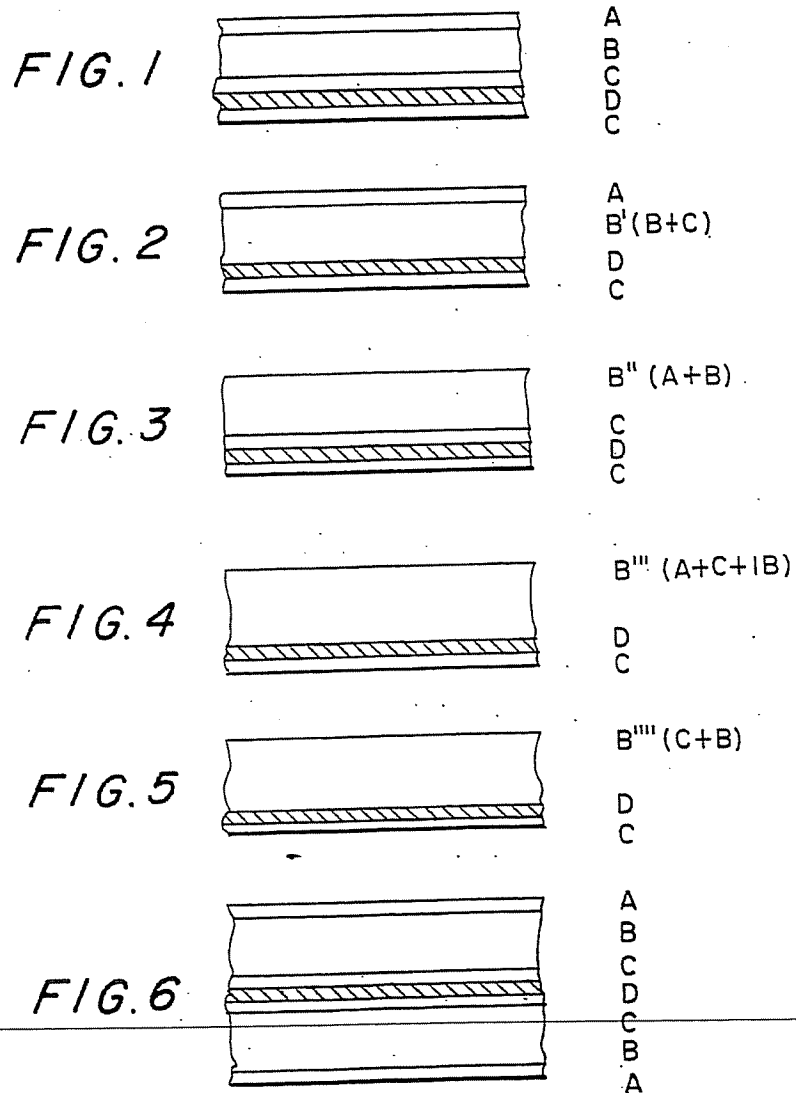
30 Claims, 6 Drawing Figures



U.S. Patent

Feb. 25, 1986

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MULTILAYER FILM WITH A GAS AND AROMA BARRIER LAYER AND A PROCESS FOR THE PREPARATION AND APPLICATION THEREOF

BACKGROUND OF THE INVENTION

The present invention relates to a multilayer, preferably sealable laminated film having a barrier layer therein, as well as to a process for its manufacture and use.

A multilayer film having a barrier layer made of a material such as that used in the present invention is described in German Offenlegungsschrift No. 26 44 209 (equivalent to British Patent Specification No. 1,567,189). The disclosed film has a multilayer structure including a base comprised of polypropylene, an intermediate layer comprising a modified polyolefin provided on the base film, and a barrier layer to reduce oxygen permeability, with a heat seal layer optionally applied to the barrier layer. The film is prepared, according to the aforementioned German Offenlegungsschrift, by applying to the transversely or longitudinally axially oriented polypropylene base film a two-layer melt comprising the polymers of the intermediate layer and the barrier layer. The composite film thus obtained is then oriented by stretching it in the transverse direction. The heat sealable layer is applied subsequently, i.e., after the preparation of the three-layer composite film, in a further step and is therefore essentially unoriented. As a result, different orientation values are obtained for the layers of the base film, the intermediate/barrier layer, and the heat seal layer, respectively.

It has now been found that the above-discussed film is frequently incapable of satisfying requirements concerning gas barrier properties, water resistance, and other physical properties, which requirements have become increasingly stringent.

To improve the sliding properties of the film disclosed by German Offenlegungsschrift No. 26 44 209, European Patent Application No. 0 062 815 describes a process to modify the outer sealing layer by means of special additives. The disclosed modification of the outer sealing layer does not improve the gas barrier properties and water resistance of the film. Furthermore, the individual layers are not oriented under the same conditions.

On the other hand, the existing sealable, multilayer films having a barrier layer comprised of ethylene-vinyl alcohol copolymers cannot be produced by extruding all of the layers simultaneously to obtain an orientation of all layers by stretching under identical conditions.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to improve the physical properties of multilayer film laminates, particularly their barrier properties against atmospheric oxygen and aromas, such as flavors, odors, etc.

It is a further object of the present invention to extend the sealing range of multilayer laminates to which are applied outer sealing layers.

It is another object of the present invention to provide improved multilayer laminates comprising one or more barrier layers containing ethylene-vinyl alcohol copolymers.

It is yet another object of the present invention to provide an improved process for producing multilayer

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film laminates, including those with barrier layers comprised of an ethylene-vinyl alcohol copolymer.

In accomplishing the foregoing objects, there is provided in accordance with the present invention a multilayer film which comprises (a) an inner barrier layer D comprised of a saponified ethylene-vinyl alcohol copolymer which contains about 15 to about 60 mole % ethylene units and which is saponified to at least approximately 90%, said inner barrier layer presenting a first surface and a second surface; (b) on at least one of said first and second surfaces, an adhesion-promoting layer C comprised of a modified polyolefin; and (c) adjacent to said adhesion-promoting layer, a layer B comprised of at least one polymer selected from the group consisting of a propylene homopolymer, a propylene copolymer, and said modified polyolefin, wherein all of the layers of the multilayer film are biaxially oriented under substantially the same stretching conditions.

In addition, there is provided a process for manufacturing a multilayer film which comprises the steps of (a) providing at least three separate melts comprising, respectively, (i) a saponified ethylene-vinyl alcohol copolymer which contains about 15 to about 60 mole % ethylene units and which is saponified to at least approximately 90%, (ii) a modified polyolefin, and (iii) one selected from the group consisting of a polypropylene homopolymer, a polypropylene copolymer and said modified polyolefin; (b) coextruding said melts to produce a multilayer composite; and thereafter (c) stretching said multilayer composite both transversely and longitudinally.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, FIGS. 1-6 each show, respectively, a cross-sectional view of a different multilayer film within the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The multilayer film of the invention has a gas and aroma barrier layer D of the aforementioned copolymer and additional layers on either side of said layer, wherein at least one of the two surface layers of the multilayer film preferably comprises a sealable outer layer A. Directly on at least one of the two surfaces of the barrier layer D, respectively, a layer C is provided, said layer C representing an adhesion-promoting layer consisting essentially or exclusively of adhesion-promoting polymers, or alternatively, comprising a mixture of polymers containing an adhesion-promoting polymer (B', B'', B''', B''').

For the purposes of the following description, one surface of barrier layer D facing optional sealable outer layer A will be arbitrarily designated the "first surface of barrier layer D." Between optional sealable outer layer A and the first surface of the barrier layer D, a first layer B is provided which is thicker than layers A and D and which performs the function of a base or support. Between the first layer B and the barrier layer D, the first adhesion-promoting layer C is present. The thickness of the layer B, which preferably amounts to about 10 to 20 microns, is essentially responsible for the mechanical properties and dimensional stability of the multilayer film, while the thickness of the optional layer(s) A and of layers C and D is relatively small, primarily because of cost considerations, and is appro-

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appropriately between about 1 micron and 3 microns (FIG. 1).

In one embodiment, layers B and C comprise a common, homogeneous layer combining both of their thicknesses, which layer (B') contains both the polymers of layer B and the polymers of the layer C (FIG. 2).

In another embodiment, layer A and the first layer B are comprised of the same polymer mixture and form a single layer which combines both of their thicknesses. Layer B in this case (B'') also has heat sealing properties. The aforementioned polymer mixture includes the heat sealing polymer material of layer A and the polymers of layer B (FIG. 3).

In yet another embodiment, only a single layer B''' is present on the first surface of the barrier layer D, which layer is both heat-sealable and is attached with sufficient strength to barrier layer D. For this embodiment, a mixture of polymers is used which includes the adhesion-promoting material of the layer C and the heat-sealing material of the layer A, and optionally, the polymers of layer B. The thickness of the single layer corresponds to the total thickness of the alternative three-layer structure of the layers A, B and C (FIG. 4).

In still another embodiment, only a single layer B''', which includes C and B, is found on barrier layer D. Heat-sealing is not used in this embodiment (FIG. 5).

The layers present on the opposite side of the barrier layer D, hereinafter designated the "second surface of D," include, for example, a layer each of A, B, and C, and are provided in configurations similar to those described for the aforementioned embodiments of the first surface of the barrier layer D (FIG. 6). Thus, combinations provided in the second surface of D of the layers A, B, and C; A and B' (B contains adhesion-promoting material); and B'' (B contains preferably heat sealing material) and C are all within the scope of the present invention.

It is preferable, however, for certain applications to eliminate the second sealable layer A and, possibly, the second layer B from the second surface of D. In such a case, a sealable surface may be produced on the second surface only at a later time, i.e., after extrusion. This may be accomplished, for example, by partial- or full-surface application effected by the printing-on of a sealable layer comprised of specially formulated polyolefins. At temperatures below 100° C., this layer is preferably sealable against itself and against other sealable layers comprised of polyolefins. This printed-on sealable layer may be located on the existing layer C or B, or it may be applied subsequently to a sealable outer layer A, if, for example, it should be discovered that the layer A is not particularly advantageous for a given special use. An ethylene-vinyl acetate copolymer is suitable as the preferred principal component for the printed-on sealable layer, since it permits the maintenance of relatively low sealing temperatures i.e., under 100° C. Alternatively, compounds that are adhesive at even lower temperatures, such as natural rubber, may be used as additional components or as other principal components. The additional components impart a sealing capability to the printed-on layer against layers of the same material with the application of pressure only. Such adhesives are known, for example, as pressure-sensitive adhesives or contact adhesives.

The barrier layer D serves as a gas barrier, in particular an oxygen or aroma barrier, and is comprised of an ethylene-vinyl alcohol copolymer with an ethylene content of about 15 to 60 mole % and a saponification

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degree of at least about 90 mole %, preferably higher than about 96 mole % and in particular approximately 99 mole %. These copolymers include, for example, ethylene-propylene-vinyl alcohol copolymers and reaction products of ethylene-vinyl alcohol copolymers with lower aldehydes or ketones, as described, for example, in German Offenlegungsschrift No. 29 31 035 and U.S. Pat. No. 4,212,936.

The ethylene-vinyl alcohol copolymers may contain water during extrusion, preferably in amounts of about 1 to 10% by weight. But to obtain a high orientation effect and, thus, a good gas barrier, it is preferable to have a water content less than 5%, preferably less than 3.5%, and in particular, less than 2% by weight or approaching zero. These values should be obtained especially during the manufacturing of the film, immediately prior to the stretching process.

The barrier layer D comprised of ethylene-vinyl alcohol copolymers may contain monomer, oligomer, or polymer substances to improve its stretchability (i.e., to influence crystallinity). The amount added in each case is controlled by the substances' compatibility (i.e., by the capacity for being worked in and mixed) with the principal component, and by the effect on the oxygen barrier. Examples of such substances are compounds containing hydroxyl and/or carbonyl groups, such as trimethylolpropane, neopentyl glycol, and polyethylene glycol, and in particular substances which have barrier properties of their own, such as polyvinyl alcohols or polyamides. Mixtures of ethylene-vinyl alcohol copolymers and about 0.5 to 50% by weight of polyvinyl alcohol with a hydrolysis degree higher than about 80, in particular higher than or equal to about 88 mole %, and a viscosity of from about 0.4×10^{-2} to about 4×10^{-2} Pa.s, in particular from about 0.4×10^{-2} to 1×10^{-2} Pa.s, are preferred.

Polyamides are compatible with ethylene-vinyl alcohol copolymers over the entire miscibility range and therefore are readily worked in. Such mixtures (blends) have already been described in European Patent Application No. 00 63 006. The films produced from them, however, are not oriented. Of the different polyamides available, the 6,12- and 6,6-copolyamides with a softening point of less than about 210° C. are especially suitable. Preferably, about 10 to 60% by weight and even more preferably about 10 to 20% by weight of a polymer or copolymer are added.

The mixing ratio is chosen so that the film is readily stretchable biaxially at the selected stretch parameters, with the gas barrier being unaffected, or being only slightly affected.

Initial extruded granules may be prepared from the granulated mixture of the polymers by known means. Preferably, the mixtures of granules are processed directly, for example, with an extrusion screw having an especially good homogenizing effect, i.e., a screw with a shear portion.

The barrier layer D comprised of ethylene-vinyl alcohol copolymers may contain further additional additives in the form of monomers, oligomers or polymers which promote adhesion to adjacent layers. Examples of such additional substances are graft-modified polyolefins, ethylene-acrylic acid copolymers, ionomers, and olefin copolymers.

In place of one barrier layer, the film may contain several oriented barrier layers which are preferably connected by an adhesion-promoting layer.

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The adhesion-promoting layers C may advantageously contain a graft-modified olefin homopolymer or copolymer, a partially saponified ethylene-vinyl alcohol copolymer with a low degree of saponification, or mixtures thereof with other polyolefins. Particularly preferred are polypropylene homopolymers or copolymers graft-modified with carboxylic acids or their anhydrides.

The polymer of layer B may be comprised of a propylene homopolymer or copolymer with a melting point of about 140° C. or higher, preferably about 150° C. or higher. Examples of suitable polymers for layer B are isotactic polypropylenes with a heptane soluble proportion of 15% by weight or less, ethylene copolymers with propylene and an ethylene content of up to 15% by weight, and copolymers of propylene with butene, pentene, hexene, heptene, octene, and/or other olefins. Mixtures of the above-mentioned copolymers may also be used. The melt flow index (MFI) of the polypropylene polymers advantageously used in this context is within a range of about 0.5 g/10 min. to about 8 g/10 min. at 230° C. and 2.16 kp/cm² (DIN 53735). The polypropylene polymers may contain additives, such as stabilizers, pigments, and low molecular weight, compatible resins or polymers.

Of the additive pigments, those lending the film a pearly lustre are preferred. Examples of such pigments are titanium dioxide, calcium carbonate, and silicon dioxide. The pigment particle size is preferably within a range of about 0.1 micron to about 20 microns, the amount added preferably in the range of about 1 to about 25% by weight. Examples of low molecular, compatible resins are petroleum resins, terpene resins, and natural oil resins obtained in the cracking of naphtha or gas oil. The resins may be hydrated and/or modified by the introduction of special monomers prior to polymerization.

The working-in of the resins to prepare mixtures to comprise layer B is effected by conventional methods. The amount of resin added is controlled by its effect on optical properties and stretchability. More than 20% by weight with respect to the propylene polymers is not necessary for processing reasons, for example, with low molecular resins, such as terpene resins.

The film is preferably sealable, while the sealable layers on either side of barrier layer D may have different thicknesses and compositions.

The optionally but preferably present sealing-layer polymer of layer A is advantageously comprised of at least one polymer selected from the group consisting of a homopolymer or a copolymer of an olefin, preferably an alpha-olefin, an ionomer, a mixture of these or of different polyolefins, and an ethylene-propylene-C_n terpolymer, where C_n denotes an alkylene monomer having n carbons, n being an integer ranging between 4 and 10. Preferably, the sealable outer layer A is comprised of a low or high density ethylene homopolymer or an ethylene copolymer. Especially preferred are ethylene-propylene copolymers and ethylene-propylene-butylene terpolymers, wherein the ethylene content is preferably from about 0.1 to about 15% by weight and the butylene content is within about 1 to about 20% by weight.

To improve its sealing capability, scratch resistance and running safety in high speed packaging machines, the sealing layer polymer of layer A may contain conventional additives, such as low molecular resins and lubricants, slip and antiblocking-agents. To optimize the

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very different requirements concerning sealing properties, combinations of copolymers and/or terpolymers with polymers, low molecular resins and polydiorganosiloxanes are preferably used. The density of the sealing layer polymers is preferably within a range of about 0.89 to about 0.96 g/cm³, the melt index within about 0.1 to about 16 g/10 min. and 2.16 kg/cm² (DIN 53735), and the softening point within about 60° to about 180° C. (DIN 1995-44), and particularly preferably between approximately 80° and 140° C.

The layer thickness of a sealable outer layer A is preferably within about 0.1 micron to about 10 microns, particularly preferably within about 1 micron to about 3 microns.

As described above, sealable layers may subsequently be applied on one or both sides to the other layers, i.e., after coextrusion. Preferably, the sealable layers have a sealing-onset temperature lower than that of layer A, or, alternatively, seal under the effect of pressure alone. These sealing layers, which after the preparation of the film may preferably be applied in a single working step during the printing of the film, may have layer thicknesses of about 0.1 micron to about 10 microns, preferably about 0.1 micron to about 5 microns.

These heat sealable layers, deposited from solutions or dispersions, may contain as principal components acrylates, ethylene-vinyl acetate copolymers, or ionomers, and the cold-sealing layers may contain natural rubber latex. They may also contain, similarly to layer A, additives such as lubricants and slip- and antiblocking-agents. To improve adhesion to the film and abrasion-resistance, the layers may be anchored on the film by means of an adhesion-promoter, for example, one containing polyurethane. A corona treatment of the film is in many cases sufficient to improve the adhesion of this additional layer or layers.

The films provided with cold-sealable layers are preferably coated on the reverse side with a adhesive lacquer, i.e., with an anti-adhesive agent. Examples of suitable adhesive lacquers are those comprised of polyamides or vinyl-containing siloxanes, which may also be cross-linked.

The multilayer film according to the present invention, when stretched at least biaxially, preferably has a total thickness of about 10 to about 100 microns, preferably about 15 to about 35 microns, wherein the major part of the thickness is made up by B layer(s).

The film according to the present invention produced by coextruding layers B, C, D, C (B optional), or A, B, C, D, C, (B and A optional) and then stretching, at least biaxially, has an excellent gas- and aroma-barrier capacity in comparison with a nonoriented film stretched at high temperatures or high atmospheric humidities, together with good mechanical properties. It is therefore outstandingly suitable for the packaging of oxygen-sensitive food, luxury, e.g., tobacco, and pharmaceutical items.

By the addition of pigments such as calcium carbonate to the polymers of the layers B or C, an opaque film is obtained.

Providing the multilayer film of the present invention with low temperature sealing or cold-sealing layers opens up new fields of application, for example, in the packaging of temperature-sensitive luxury items.

The control of gas permeability by means of layer thickness, formulation, and degree of stretching, together with the provisions of a wide sealing range, permit other industrial applications. Examples are the